PARAMAGNETIC RESONANCE EFFECT IN VISCOELASTIC MATERIALS

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Introduction

During the period covered by this grant, the EPR equipment has been purchased, received, and put into operation. A variable temperature accessory has been installed that makes it possible to maintain and control the temperature at any value between $-185^{\circ}C$ and $+300^{\circ}C$. Facilities have also been constructed to control the atmosphere of the sample in the microwave cavity. A hydraulic loading frame, pump, controls, etc. have been designed and constructed for tensile loading the samples in the microwave cavity. Load, strain, and EPR spectra can be simultaneously recorded on a built-in oscillograph system. The experimental set up is illustrated in Figure 1.

This report will describe some of the early results obtained in studying fracture mechanisms with this equipment and apparatus.

Background

Intensive research efforts on the study of fracture in viscoelastic materials has been stimulated in recent years by the wide use of and interest in solid propellants, plastics, gels, and other viscoelastic materials. (1-6) In this country most of the experimental work has dealt with viscoelastic failure from a macroscopic rather than a molecular point of view. However, recently S. N. Zhurkov of the USSR Academy of Sciences has reported studies using electron paramagnetic resonance (EPR) techniques to measure the number of bonds broken during mechanical fracture in polymers. (7-10) This technique makes it possible to study fracture on a molecular basis in covalently bonded materials.

Before proceeding with a description of our experiments, it might be appropriate to give a very brief descriptive review of the principles of EPR for the readers of this report who might not be familiar with its principles or its uses. (More complete and thorough descriptions of EPR, its uses, and applications can be found in several recent books and reviews.) (11-15) EPR deals with systems of elementary particles which have a net electronic movement (unpaired electron spins). It is a form of absorption spectroscopy in which transitions are induced between energy levels arising from Zeeman-type splitting in an assemblage of paramagnetic electrons. The (Zeeman) Hamiltonian of an isolated electron with spin $\bar{s}$ placed in a magnetic field $\bar{H}$ is

$$\mathscr{H} = g\beta s \cdot \bar{H} \tag{1}$$

where g, the "spectroscopic splitting factor," is 2.0023 for a free electron and β is the Bohr magneton. If the magnetic field direction is chosen along the z-axis, the normalized spin wave functions of the electrons have z-components m = +1/2 or m = -1/2, corresponding to energies of

$$E_m = g\beta H_z m \; ; \quad m = \begin{cases} +1/2 \\ -1/2 \end{cases} \tag{2}$$

At thermal equilibrium, the distribution of electrons in these two energy levels is given by Boltzmann statistics to be:

$$\frac{N+}{N-} = \exp(-\Delta E/kT) \tag{3}$$

where ΔE is given by the Plank relation and Equation 2 as

$$\Delta E = h\nu = g\beta H_z \tag{4}$$

Transitions between the levels may now be induced by incident radiation of frequency, $\nu = g\beta H_z/h$, which is right circularly polarized along H_z. These transitions occur in either direction with equal probability, but since the lower state is more densely populated (Equation 3), the upward transitions

outnumber the downward. Thermal equilibrium as given by Equation 3 is maintained via spin-lattice relaxation: electrons in the upper state relax to the lower state by giving their excess energy to their surroundings. This produces a net energy loss from the incident radiation which may be detected with suitable instrumentation.

Experimentally, it is generally convenient to supply incident radiation at a fixed frequency and then sweep the magnetic field through the range of interest. Energy absorbed by the sample when Equation 4 is satisfied may then be plotted versus field strength. In order to enhance the sensitivity, most EPR spectrometer systems modulate the field and phase-detect the absorption curve so as to produce a first derivative representation.

The study of free radical chemistry is currently a very active research area and EPR spectroscopy has become a standard analytical technique in this field. (16-18) Many different types of degradation processes have been investigated rather extensively, including such processes as thermal degradation, anionic degradation, ultraviolet irradiation, neutron bombardment, γ- and x-ray irradiation. etc. Strangely, the study of mechanical degradation (i.e., the breaking of polymeric bonds by mechanical processes) using EPR technique seems to have been neglected until the work of Zhurkov and his colleagues. (19-21)

Since the unpaired electrons of the free radicals (broken bonds) sense not only the presence of the applied magnetic field but are capable of electrical and magnetic interaction with nuclei and electrons of their surroundings, EPR provides not only a means of determining the number of free radicals (broken bonds) leading to fracture, but in principle at least,

makes it possible to determine which bonds are broken. The potential

of such a tool in furthering the understanding of fracture mechanics is

obvious.

Experimental Procedure and Results

The first task undertaken in this EPR-fracture study was to verify

Zhurkov's fracture experiment and to place mechanical degradation into

context with studies on other types of degradation reported in the liter-

ature. Since free radicals produced by γ-irradiation have been studied

rather extensively, tests were conducted on several different polymeric

materials (Nylon, Solithane, PMMA, etc.) subjected to varying amounts of

γ-irradiation from a Co^{60} source. These are being compared with the spec-

tra from free radicals formed from mechanically broken bonds. It is thought

that comparisons of the differences and similarities of these spectra and

their annealing and recombination rates will be helpful in identifying the

free radical species and, particularly, in investigating the role played

by the newly-formed fracture surfaces. The early result of these studies

while still preliminary in nature certainly indicates that this work should

be very rewarding and produce considerable enlightenment and insight into

fracture mechanisms.

The Varian E-3 EPR Spectrometer system employed in the studies operates

at a microwave frequency 8.8 to 9.6 gHz and a field modulation frequency of

100 kHz. All the tests were made at low microwave power (∿1 mw) to avoid

saturation. Typical instrument settings for the data to be presented later

were: field modulation, 10 gauss; sweep rate approximately 200 gauss per

minute; and recorder time constant 1/2 sec.

Bonds were ruptured (free radicals formed) by three different methods: (1) γ-irradiation, (2) grinding, and (3) tensile fracture. As noted above, the first of these was done to establish a standard with which to compare the others since γ-irradiation had been studied quite extensively and was, therefore, quite well understood. The grinding work allowed the accumulation of large amounts of rupture surface and, therefore, strong signals, and in addition facilitated operation at low temperatures, thereby retarding annealing, recombination, and proton or free radical migration. An understanding of the kinetics involved in these processes would hopefully make it possible to extrapolate back to the time of rupture in the tensile tests. The fracture studies which are reported herein are preliminary in nature; they will eventually be the main goal of this research team effort, and will be thoroughly and systematically studied in the future.

The materials for the γ-irradiation and grinding studies was commercial grade of reasonably good purity purchased locally. Efforts are presently being made to obtain better controlled samples from several manufacturers. The tensile samples were nylon fibers provided by Allied Chemical Corporation. X-ray fluorescence of these fibers indicated that the only inorganic ions present in substantial amounts were copper, 61 ppm; iodine, 0.2 per cent; and all other metals less than 2 ppm.

The samples to be irradiated were cut to size, allowed to anneal at room temperature for at least 24 hours, and then irradiated by a Cobalt 60 source. Irradiation was done both at liquid nitrogen and room temperature. Typical spectra are shown in Figure 2. Due to the excellent sensitivity and ease of operation of the new E-3 spectrometer, even the early tests not only agreed well with published results, but generally improved upon them in terms of

resolution and ease of interpretation. This work enabled the research team to acquire the experimental techniques peculiar to EPR-free radical work, and to become familiar with the literature pertaining to non-mechanical degradation. Using carbide grinders, several different types of polymers were ground in various atmospheres, both at liquid nitrogen and room temperature. The spectra obtained from these powders are now being correlated with those obtained from irradiated samples; typical grinding spectra are shown in Figures 3 and 4.

After preparation by grinding or irradiation, the samples were stored at liquid nitrogen temperatures until use. No detectable difference in signal shape or strength could be detected between samples studied immediately upon preparation and those stored at LN temperatures up to two weeks (the longest storage attempted).

Annealing was studied as a function of atmosphere and temperature, and was found to be much more atmosphere and temperature sensitive for the bonds broken by grinding than in the irradiated samples. This is likely due to the fact that radicals produced by grinding lie close to the surface; a systematic study of this effect which is presently underway should make it possible to determine the depth of damage (free radical formation) at newly-formed fracture surfaces. This study should considerably extend the understanding of the character of surfaces created in fracture.

It is significant to note that the grinding studies may make possible the experimental determination of the energies of newly-formed fracture surfaces. The grindings' surface area can be determined by a sorptometer, so the EPR spectrometer data yields the number of broken bonds formed per square cm of new surface area.
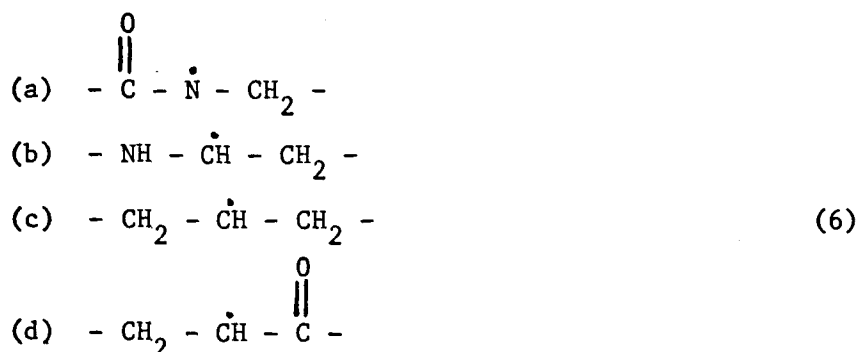
We have begun the analysis and, in the case of Nylon 6 at least, we are already in a position to make a few definitive statements. The results to be presented here are similar to those of a paper prepared for presentation at the 14th Sagamore Army Materials Research Conference in August 1967.

Figures 5 through 7 are typical EPR spectra for Nylon 6. In each case the spectrum was recorded at $-160^{\circ}C$ after annealing in helium at $-40^{\circ}C$. They represent γ-irradiated solid material grindings allowed to anneal at room temperature until the signal produced by grinding had completely vanished and then irradiated and material ground under liquid nitrogen and the free radicals so formed studied directly. Figures 7-10 are similar to Figs. 5-7 except measurement and annealing were accomplished in oxygen.

Discussion of Results

The spectra produced in the present series of tests on ground and irradiated nylon generally consist of five peaks, as indicated in Figure 11a. The central peak was observed to obey different kinetics than the other four, sometimes being almost non-existent and sometimes exceeding the other peaks in intensity by several fold. It is possible to interpret this spectrum as a quartet with a superimposed singlet.

It has been suggested (22) that the spectra of the type shown in Figure 11a is due to free radicals arising from proton removal; there are four such radicals possible in the polyamide chain:
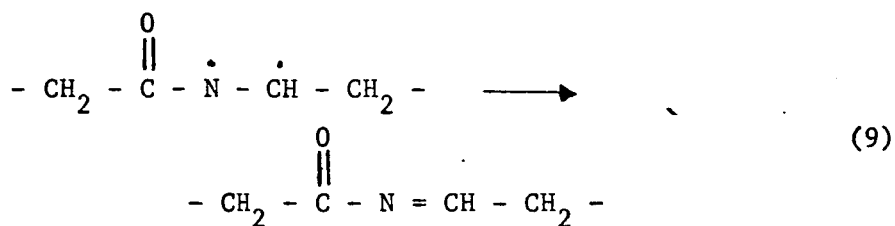
$$
\begin{array}{lll}
\text{(a)} & \quad -\overset{\overset{\displaystyle O}{\|}}{C} - \overset{\displaystyle \bullet}{N} - CH_2 - & \\[4mm]
\text{(b)} & \quad - NH - \overset{\displaystyle \bullet}{C}H - CH_2 - & \\[4mm]
\text{(c)} & \quad - CH_2 - \overset{\displaystyle \bullet}{C}H - CH_2 - & \text{(6)} \\[4mm]
\text{(d)} & \quad - CH_2 - \overset{\displaystyle \bullet}{C}H - \overset{\overset{\displaystyle O}{\|}}{C} - &
\end{array}
$$

-7-

Choice of a particular radical is made less ambiguous by the fact that hyperfine splitting with the σ-proton is markedly anisotropic with respect to the magnetic field direction while the π-proton splittings are isotropic (23). On the basis of previous work along these lines (23-24), the radical responsible for the quartet shown in Figures 1 through 7 is taken to be:

$$
\begin{array}{c}
O \\
\parallel \quad\quad\quad \cdot \\
- C - NH - CH - CH_2 -
\end{array}
\quad\quad\quad (7)
$$

This interpretation is consistent with others in the literature. (25-28) The only effect of the -NH- group is a broadening of the other lines due to unresolved coupling with the N^{14} nucleus (23,27,29). Previous theoretical and experimental work indicates that the π-splittings are ∿25 gauss while the σ-splittings vary with orientation from 15 to 30 gauss. In general, a triplet with a doublet substructure would be produced, but in the unoriented samples tested here, the π- and σ-splittings are roughly equal, thus explaining the observed quartet. The central singlet is attributed to the addition of a hydrogen atom to the carbonyl group to give the radical (25):

$$
\begin{array}{c}
O \\
\vert \\
- CH_2 - C - NH - CH_2 - \\
\vert \\
H
\end{array}
\quad\quad\quad (8)
$$
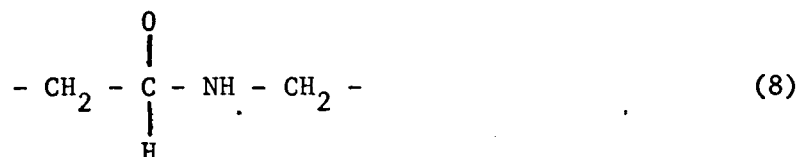
It has been proposed that the situation further develops as follows: radical migration along the polymer chain (hydrogen transfer) allows two radicals to combine to produce unsaturation (22):

$$
\begin{array}{c}
O \\
\parallel \quad \cdot \quad\; \cdot \\
- CH_2 - C - N - CH - CH_2 - \quad\longrightarrow \\
\\
O \\
\parallel \\
- CH_2 - C - N = CH - CH_2 -
\end{array}
\quad\quad\quad (9)
$$

The presence of oxygen, even in small amounts, introduces a marked asymmetry into the EPR spectra. (29-34) This effect seems due to the formation of chain peroxy radicals of the form

$$- CH_2 - CH(\overset{\bullet}{OO}) - CH_2 - \qquad (12)$$

The asymmetric nature of the peroxy spectrum reflects the anisotropy in that radical's g-value. (33) Apparently, the degeneracy of the two non-bounding p-orbitals in the oxygen is lifted by some unspecified mechanism, allowing the admixture of some orbital angular momentum via spin-orbit coupling. (34) This dequenching of orbital angular momentum along the direction of the 0-0 bond is reflected in a shift of $g_{||}$ to a substantially higher value than the free spin value of 2.0023. (32) Since $g_{\perp}$ is close to the free spin value, the peroxy radical will produce two EPR absorption lines, the resultant of which is asymmetric (Figure 11b).

It appears that the same radicals are present in both the irradiated material and the grindings. Both produce spectra whose g-value is approximately 2.00, typical of free radicals in polymers. The singlet, however, appears much more abundant in the mechanically degraded material. It may be that sufficient local heating is generated in the grinding operation to produce such a change in the spectra, even though such an effect should have been minimized by the fact that all grinding operations were conducted under liquid nitrogen.

Some care must be exercised in interpreting the free radicals represented by the spectra of Figures 5 through 10 as being those formed by the initial bond rupture, either during mechanical breakdown or irradiation. The concept of radical migration implies that there exists certain sites of higher stability along the polymer chain at which the migrating radical will have greater residence times. It will be noted,

for example, that the spectra obtained were not identified above with radicals representing chain scission. One would expect that if bond rupture is the controlling mechanism during fracture as has been suggested (9,10) that backbone scission would very likely take place. If so, the free radicals so formed must be sufficiently mobile, even at liquid nitrogen temperatures, to form the more stable radicals within a few minutes. (8)

From the above, it would appear to the authors that in Nylon 6 the following possibilities exist:

1. Chain scission does not occur during polymeric degradation, i.e., the proton removal mechanism used to interpret the observed EPR spectra is the only mechanism dominant during degradation. This seems unlikely; it is difficult to envision tensile fracture without chain rupture and the γ-rays used in the irradiation studies certainly contain more than enough energy to break bonds in the polymeric solid indiscriminantly.

2. Chain scission does take place and the radicals (or bi-radicals) so formed are represented in the EPR spectra of the degraded solid. For instance, the bi-radical

$$- \overset{\bullet}{C}H_2 \ . \ . \ . \ \overset{\bullet}{C}H_2 -$$
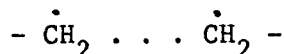
would produce a quintet if one assumes that each electron interacts equally with each of the four π-protons. This possibility, however, has been discounted by the authors since it fails to account for the independent nature of the central EPR line. In addition, the placement of the radical adjacent to the amine group in irradiated polyamides has been rather unambiguously verified in the literature.

3. Chain scission does take place, but the radicals so formed are
   unstable and soon evolve to more stable sites adjacent to the amine
   groups. The authors feel that this constitutes the most consis-
   tent and reasonable explanation of the phenomenon. Since this radi-
   cal migration process is active even at liquid nitrogen temperature,
   work at even lower temperature (e.g., liquid helium) may permit the
   stabilization and identification of those bonds which are actually
   broken during fracture.

Previous work on EPR signal decay has been interpreted in terms of first-
order kinetics where the reaction was controlled by the diffusion of a react-
ing species such as oxygen and by second-order kinetics where migration and
recombination of free radicals were the decay mechanisms. (22,27) Figures 12
and 13 indicate that the present studies are not inconsistent with such a
model if it is assumed two species are present with different decay rates.
The relative concentrations shown in these figures were obtained by numerical
double integration of the EPR spectra and comparisons with a "Pitch" standard.
At least part of the scatter in these figures can be attributed to some
machine problems encountered in this integration. One rather anomalous
effect was noted, however; from a study of the spectra produced, it appeared
that immediately upon warming, the singlet grew rapidly at the expense of
the quartet. After the first few minutes, the singlet appeared to decay
more rapidly than the quartet.

In helium the irradiated powder and solid material appeared to obey
very nearly the same kinetics. In oxygen the signal in the powder annealed
away more rapidly due to the shorter diffusion distance for the oxygen.
The free radicals produced by grinding disappeared more rapidly than those

formed by irradiation which was undoubtedly due to the fact that the radicals were produced in much greater abundance at the surface. The shorter diffusion path and surface diffusion accelerated both the development of peroxy radicals and recombination. A systematic study of this effect should make it possible to determine the depth of damage at new surfaces produced by grinding. Such a study is presently underway.

The grindings were studied under 50 power magnification on a metallograph. They were highly irregular in shape but typically had dimensions of the order of 10^{-3} to 10^{-1} mm. The surface area as measured on a Perkin-Elmer-Shell sorptometer was 3,000 to 4,000 cm^2/gm. This would correspond roughly to 3×10^{14} unpaired spins formed per square cm of new surface created.

The tensile test represented in Figure 14 was conducted in air at room temperature. Under these conditions the decay of the signal is quite rapid resulting in an equilibrium concentration at any given stress. Figure 11a shows the equilibrium spectrum at three different load levels. The difference in line shapes is likely partially due to orientation effects. Figure 11b shows the engineering strain and increase in peak height of the EPR spectra as functions of time. The peak height should be roughly proportional to the free radical concentration. In these figures approximately eight seconds was required to increase the load from zero to its final value.

This work is presently being continued and extended. It should provide a valuable tool for studying fracture mechanisms under various types of loadings, atmospheres, and other conditions and an excellent means of studying and checking the different theories and models proposed to explain polymeric fracture.

Conclusions

The work to date has demonstrated the real utility of EPR in studying fracture. The authors are looking forward with anticipation to the continuation and expansion of these research efforts. They feel that, among others, the following areas of investigation should be undertaken:
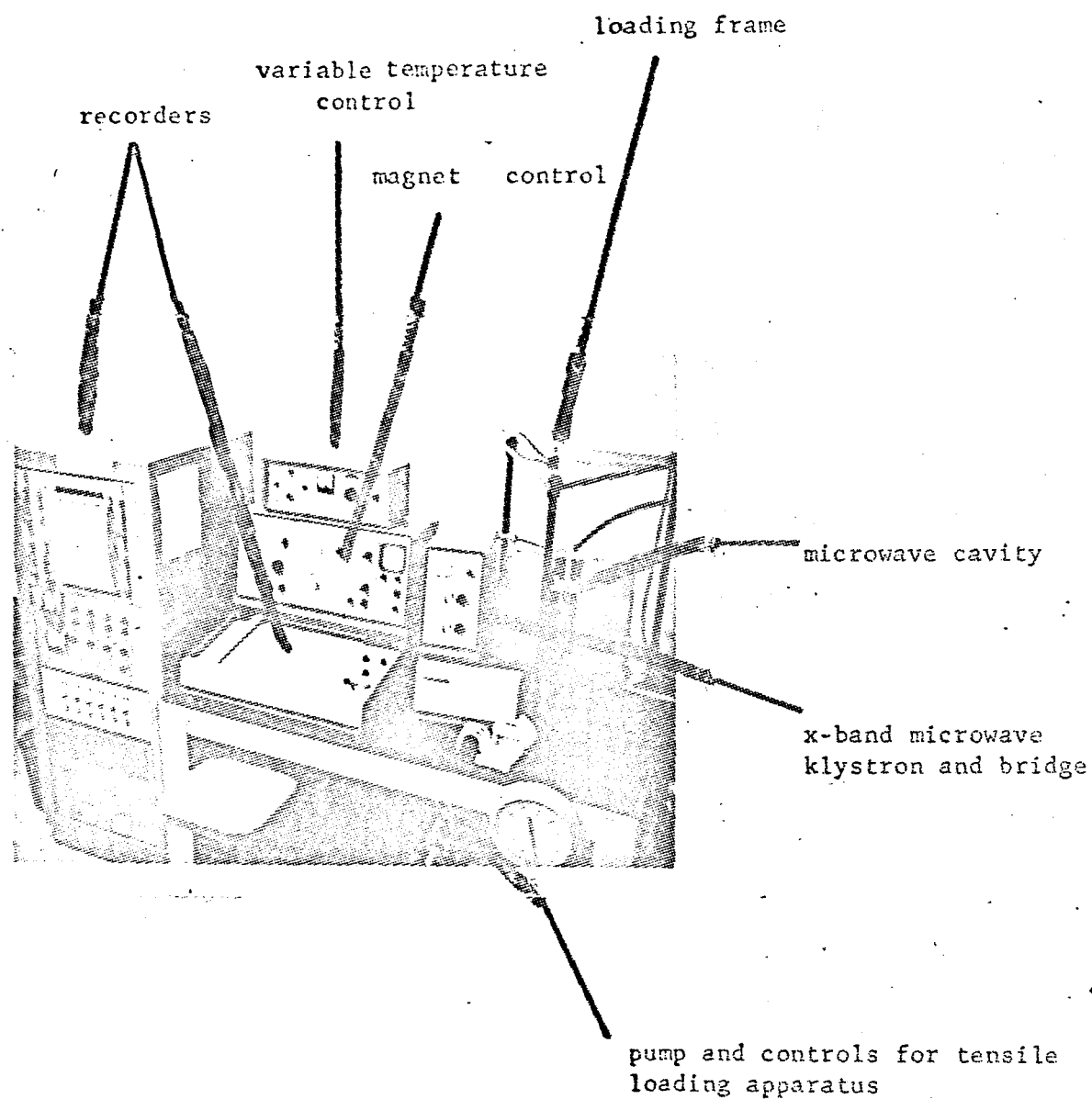
1. Extend the measurements of the number of free radicals formed per unit area of new surface to different particle sizes, to other materials, and as functions of crystallinity, temperature, etc.

2. Determine free radical concentration as a function of depth on newly-formed surfaces.

3. Make a systematic study of viscoelastic tensile fracture as functions of temperature, crystallinity, state of stress, loading history, etc.

4. Extend the studies along the lines suggested in the body of this progress report.

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recorders

variable temperature
control

loading frame

magnet   control

microwave cavity

x-band microwave
klystron and bridge

pump and controls for tensile
loading apparatus

Figure 1. EPR Equipment, Loading Apparatus, Recorder, and Controls

NYLON 6

SOLITHANE
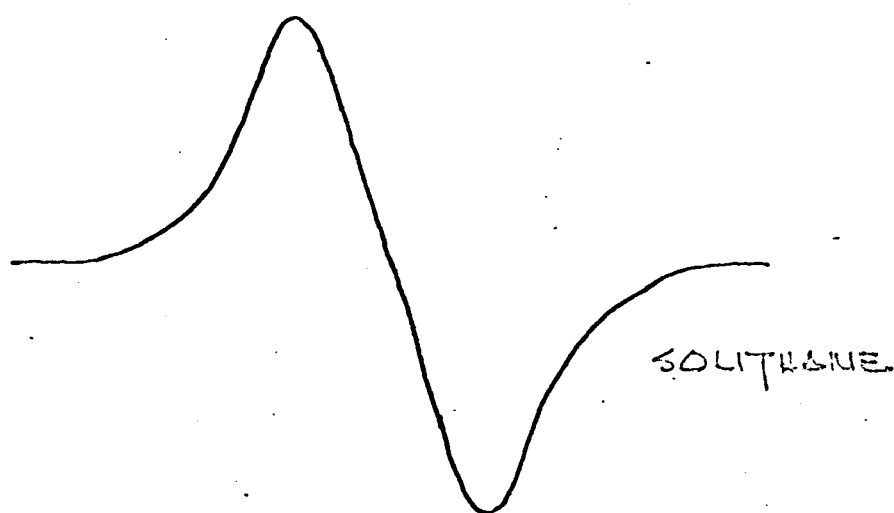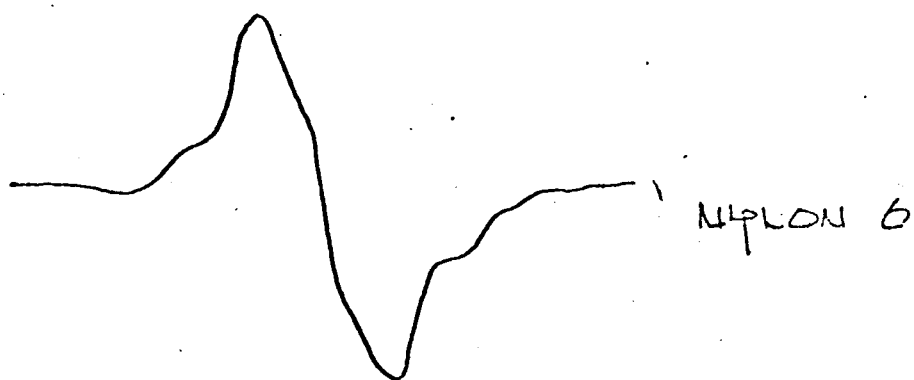
Figure 2. Typical EPR spectra produced by γ-irradiation.

POLYPROPYLENE

NYLON 6

POLYETHYLENE
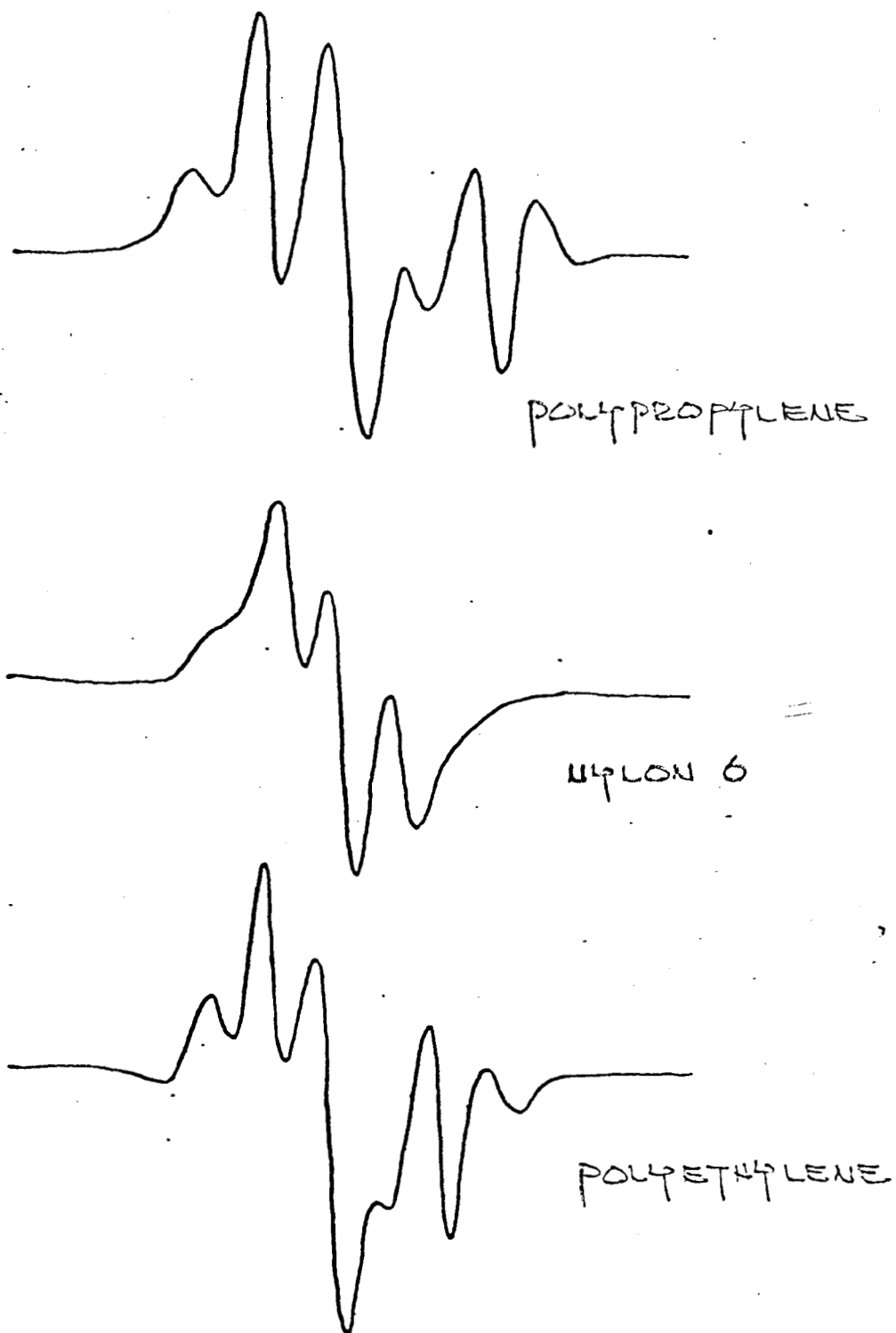
Figure 3. Typical EPR spectra produced by grinding.

SOLITHANE

POLY METHYL METHACRYLATE

Figure 4. Typical EPR spectra produced by grinding.
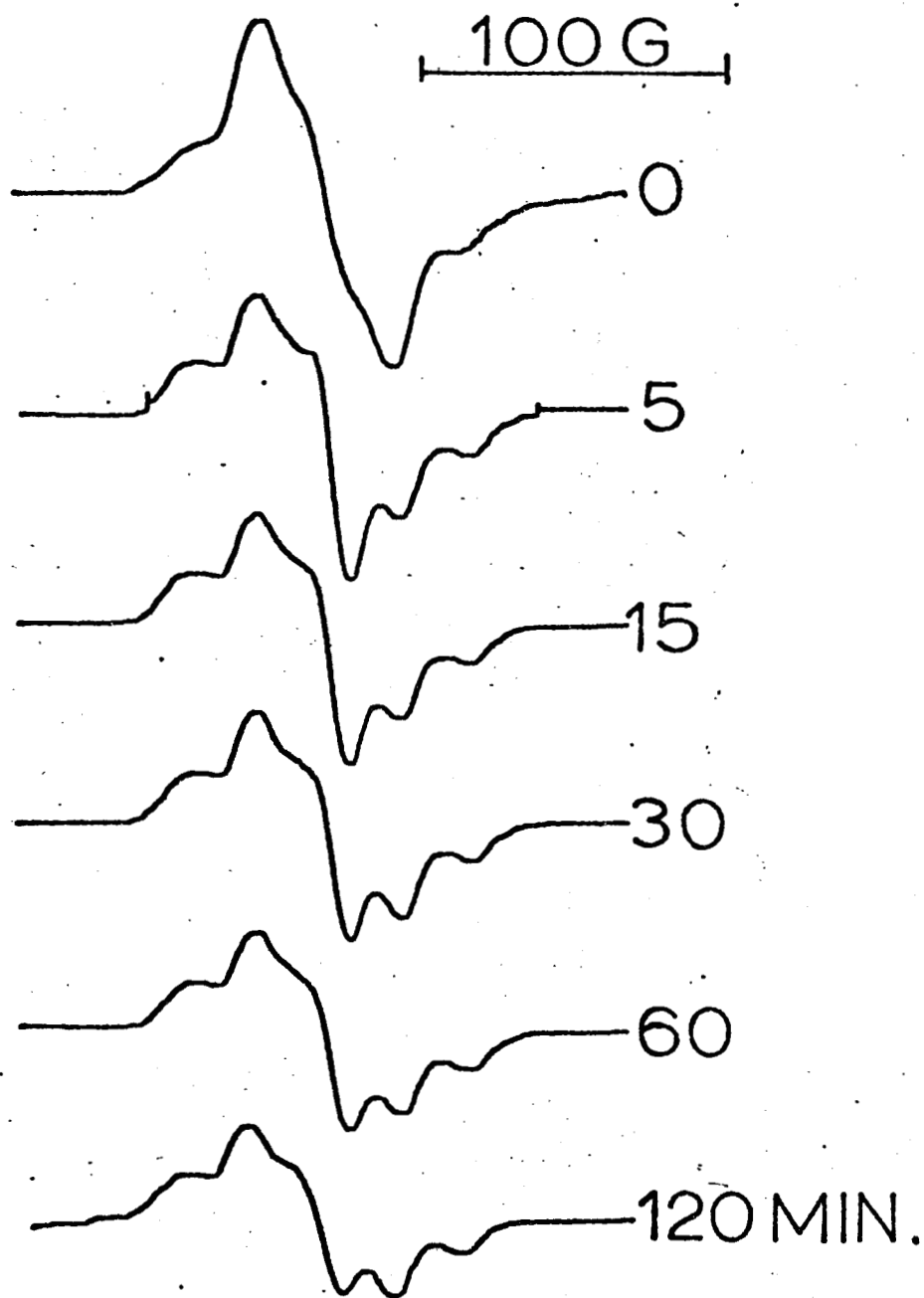
Figure 5. Typical EPR spectra for Nylon 6 after γ-irradiation. Specimen was a solid piece with a mass of approximately 0.021 grams. The numbers to the right are the total times the sample was maintained at -40°C. The testing was conducted in a helium atmosphere.
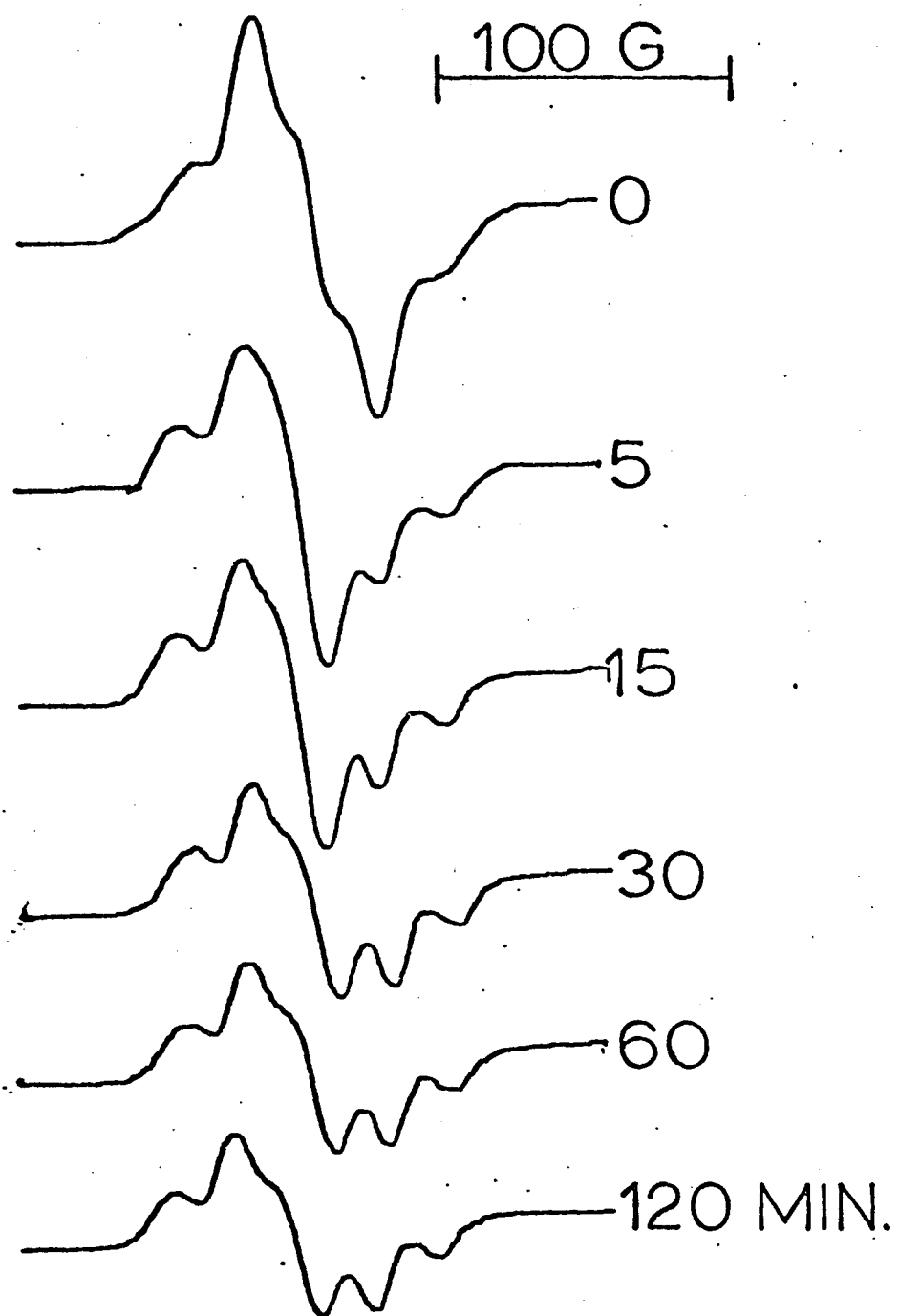
Figure 6. Typical EPR spectra for Nylon 6 grindings after irradiation. The sample was ground, allowed to anneal until it gave no EPR signal, and then irradiated. The numbers to the right are the total times the sample was maintained at -40°C. The testing was conducted in a helium atmosphere.
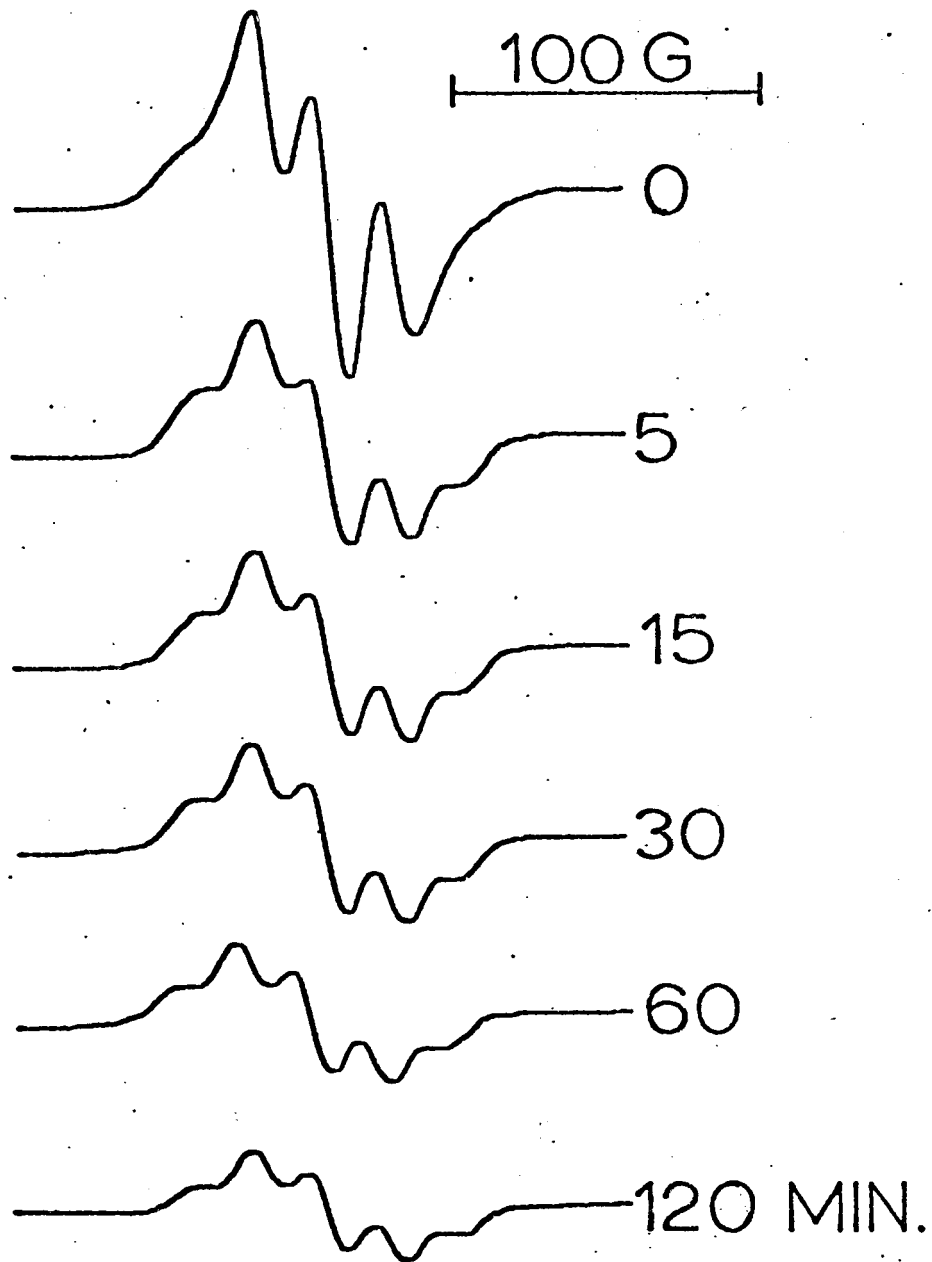
Figure 7. Typical EPR spectra resulting from the grinding of Nylon 6. The numbers to the right are the total times the sample was maintained at -40°C. The testing was conducted in a helium atmosphere.
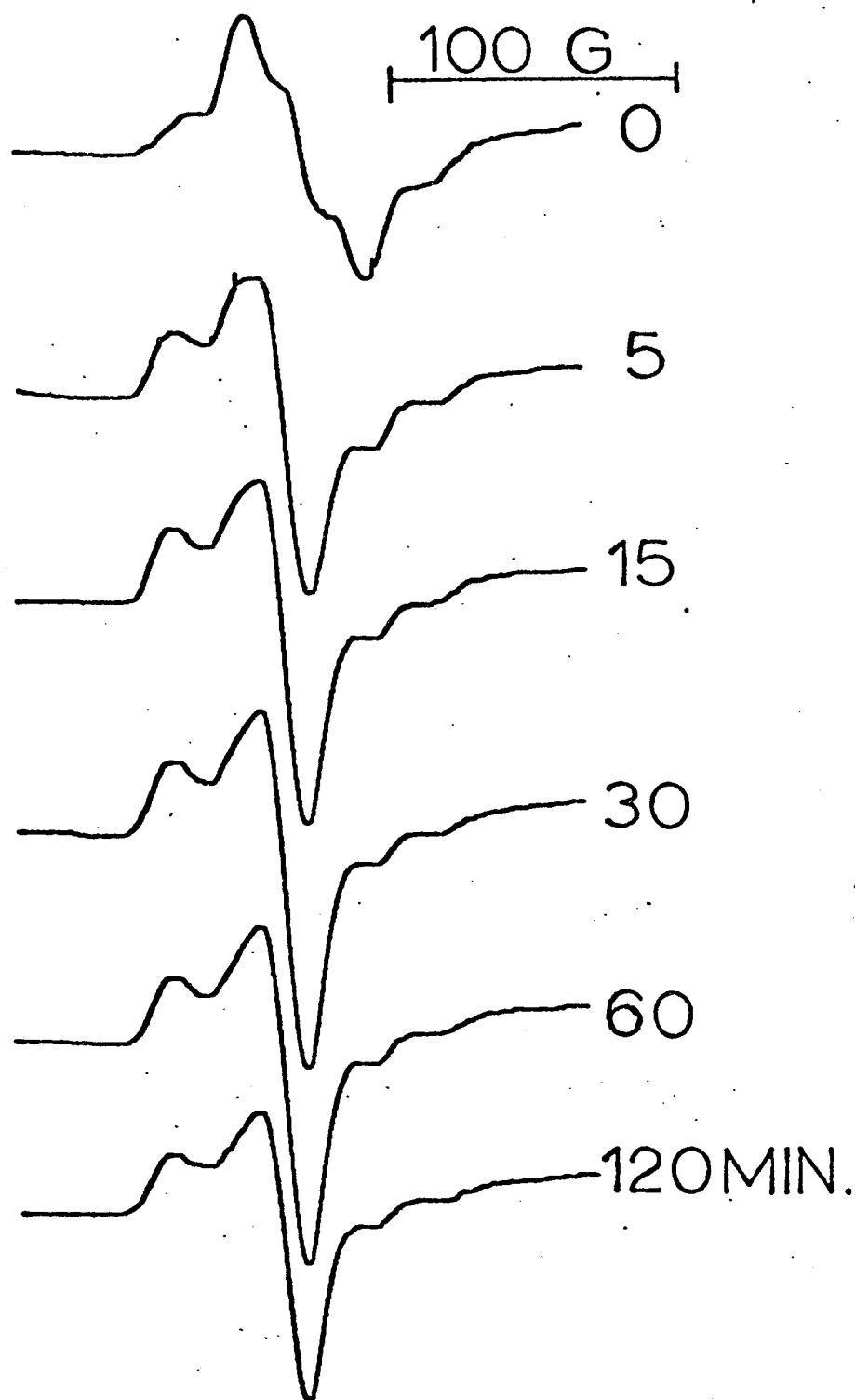
Figure 8. Typical EPR spectra for Nylon 6 after γ-irradiation. Specimen was a solid piece with a mass of approximately 0.021 grams. The numbers to the right are the total times the sample was maintained at -40°C. The testing was conducted in an oxygen atmosphere.
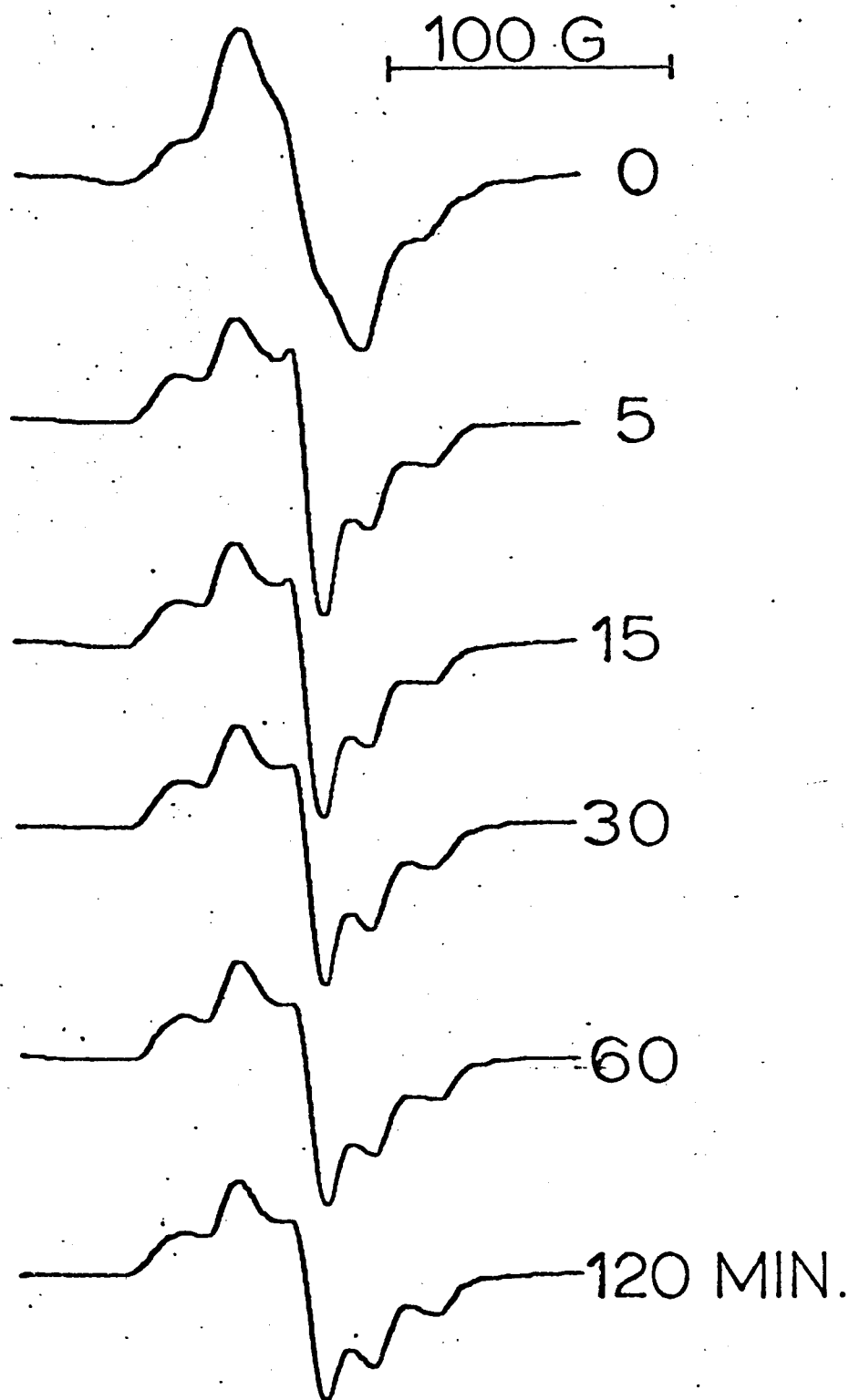
Figure 9. Typical EPR spectra for Nylon 6 grindings after irradiation. The sample was ground, allowed to anneal until it gave no EPR signal, and then irradiated. The numbers to the right are the total times the sample was maintained at -40°C. The testing was conducted in an oxygen atmosphere.
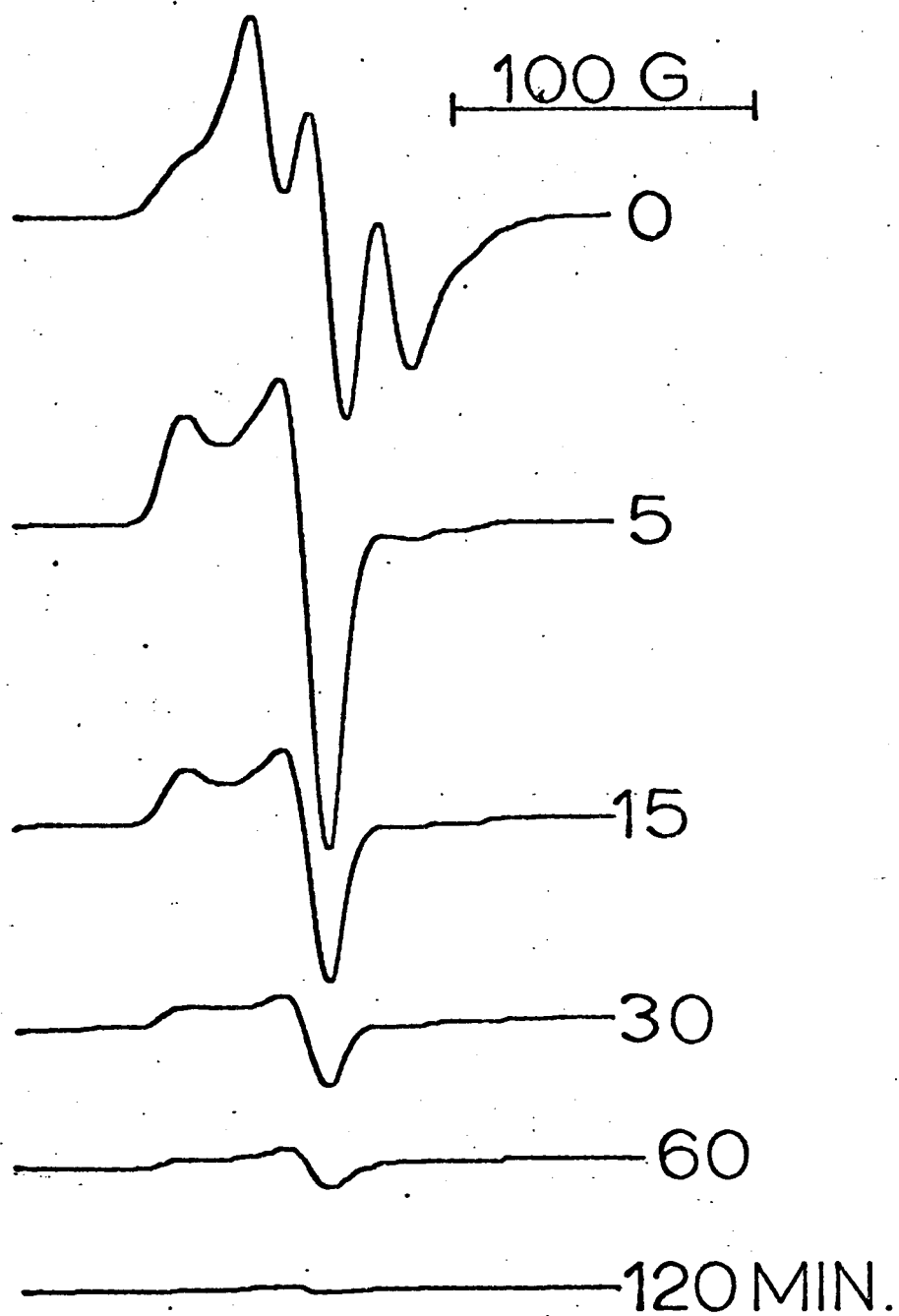
Figure 10 Typical EPR spectra resulting from the grinding of Nylon 6. The numbers to the right are the total times the sample was maintained at -40°C. The testing was conducted in an oxygen atmosphere.
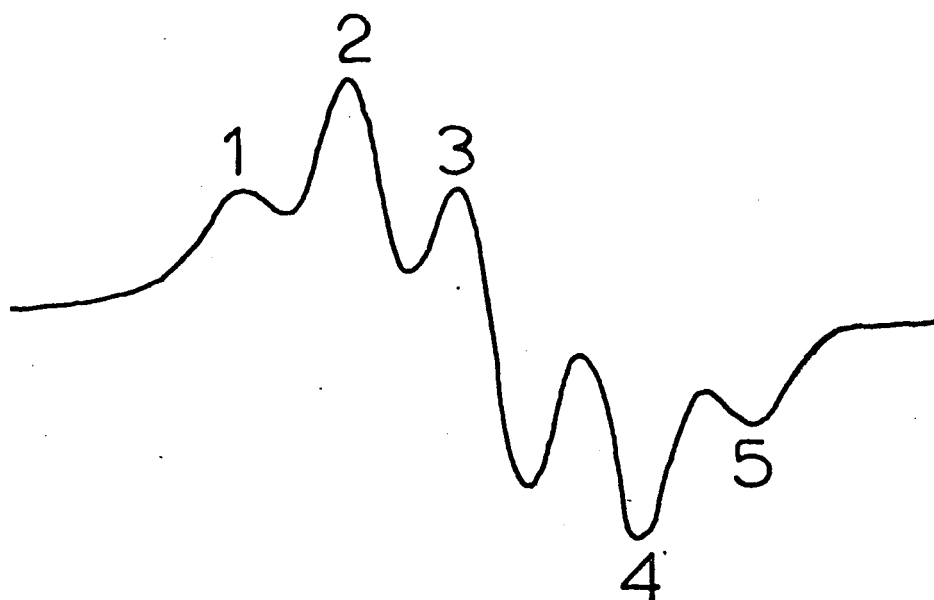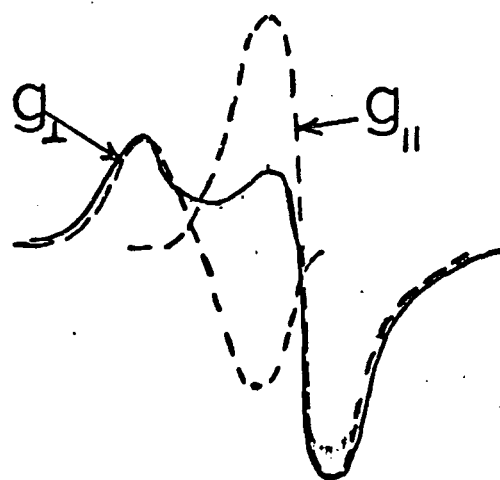
Figure 11a. Typical five peak EPR spectra.

Figure 11b. Asymmetric peroxy radical resulting from addition of $g_\perp$ and $g_{||}$.
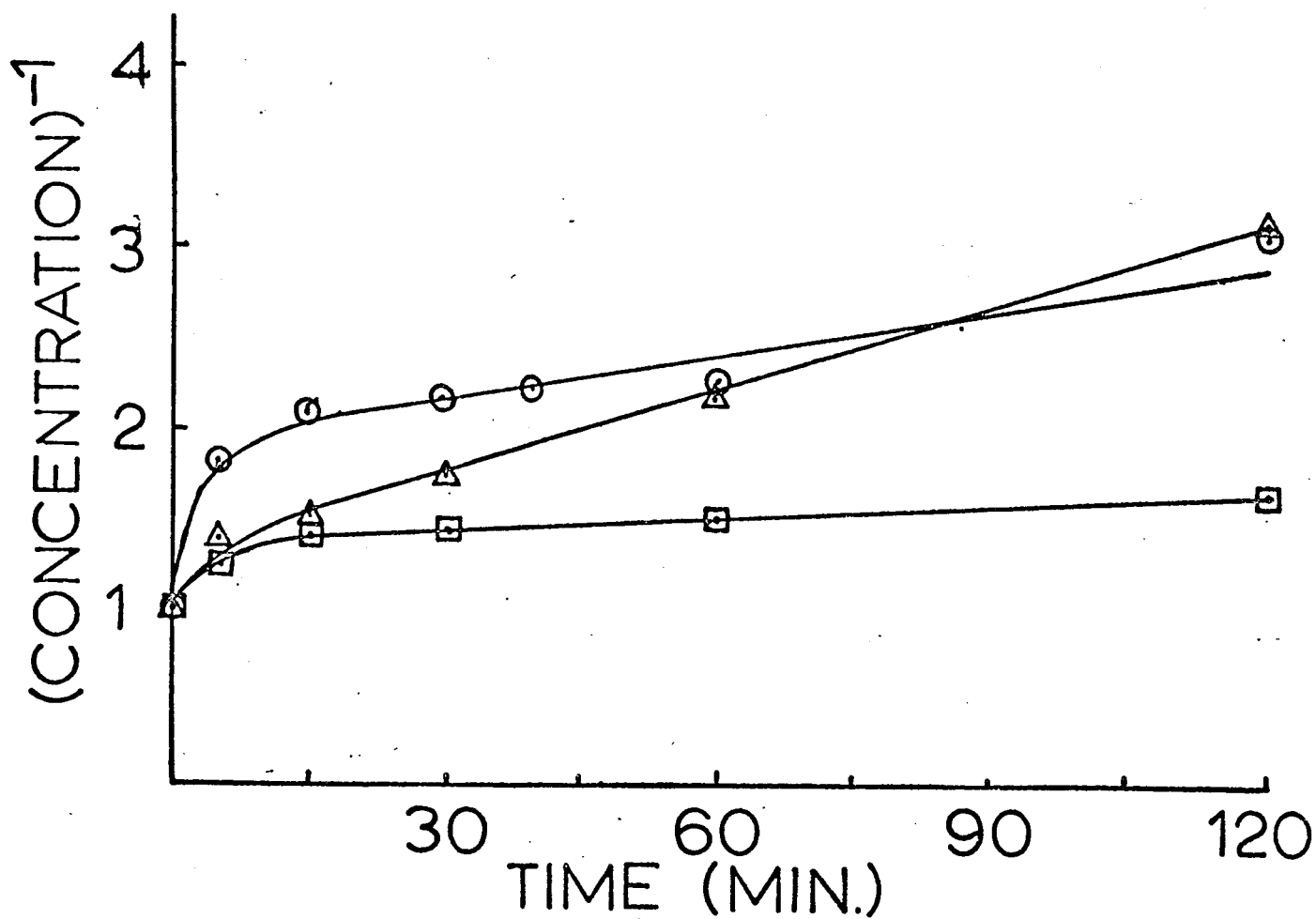
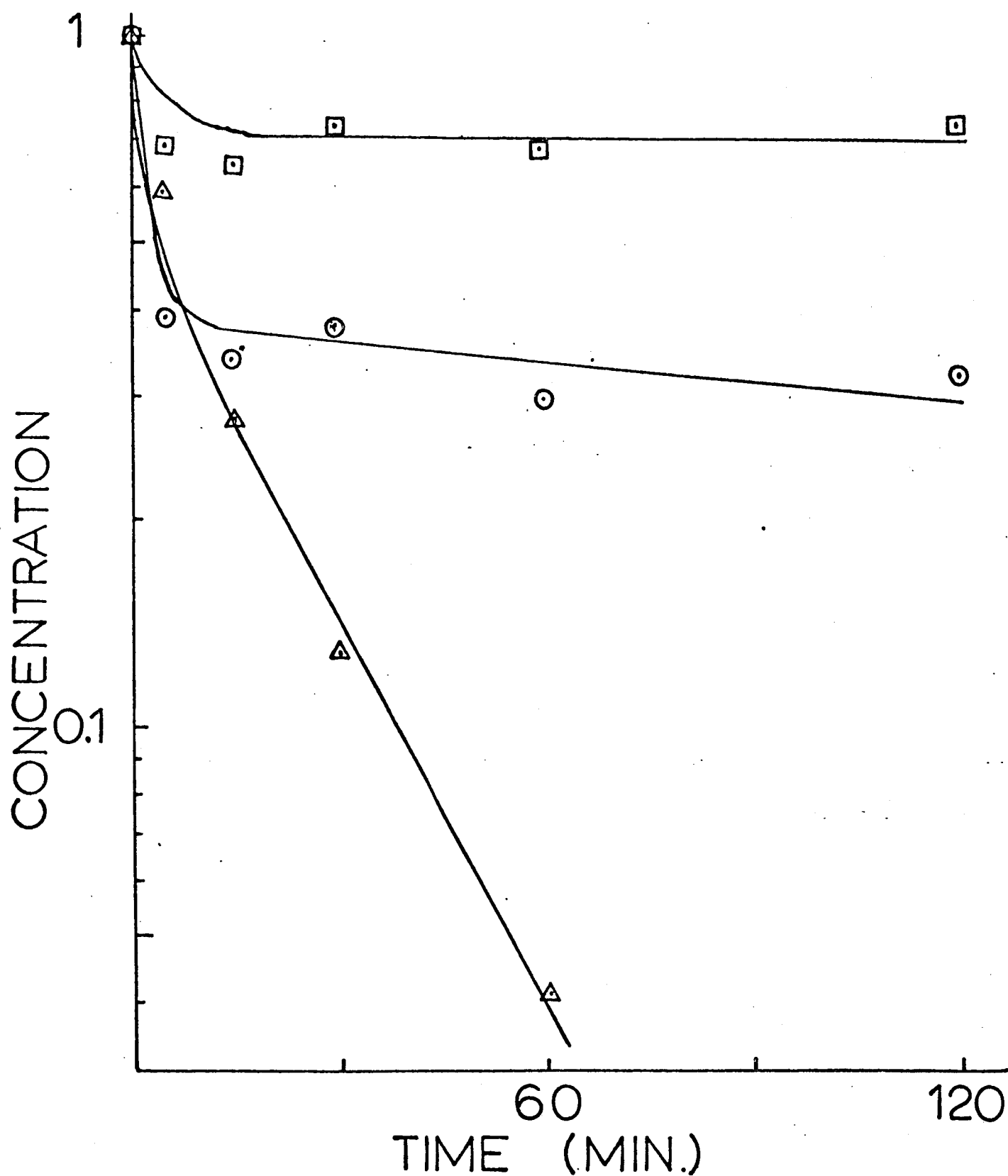Figure 12. The decay in free radical concentration of Nylon 6 in a helium atmosphere vs time at -40°C. ⊡ solid, Y-irradiated; ⊙ grindings annealed and Y-irradiated; △ grindings. The concentrations are normalized to their initial values which were roughly: ⊡, 5×10^{17}, ⊙, 3×10^{17}, and 13×10^{17} spins/gram.

Figure 13. The decay in free radical concentration of Nylon 6 in an oxygen atmosphere vs time at -40°C. ⊡ solid, γ-irradiated; ⊙ grindings annealed and γ-irradiated; △ grindings. The concentrations are normalized to their initial values which were roughly: ⊡, 3 x 10¹⁷, ⊙, 2 x 10¹⁷, and 7 x 10¹⁷ spins/gram.
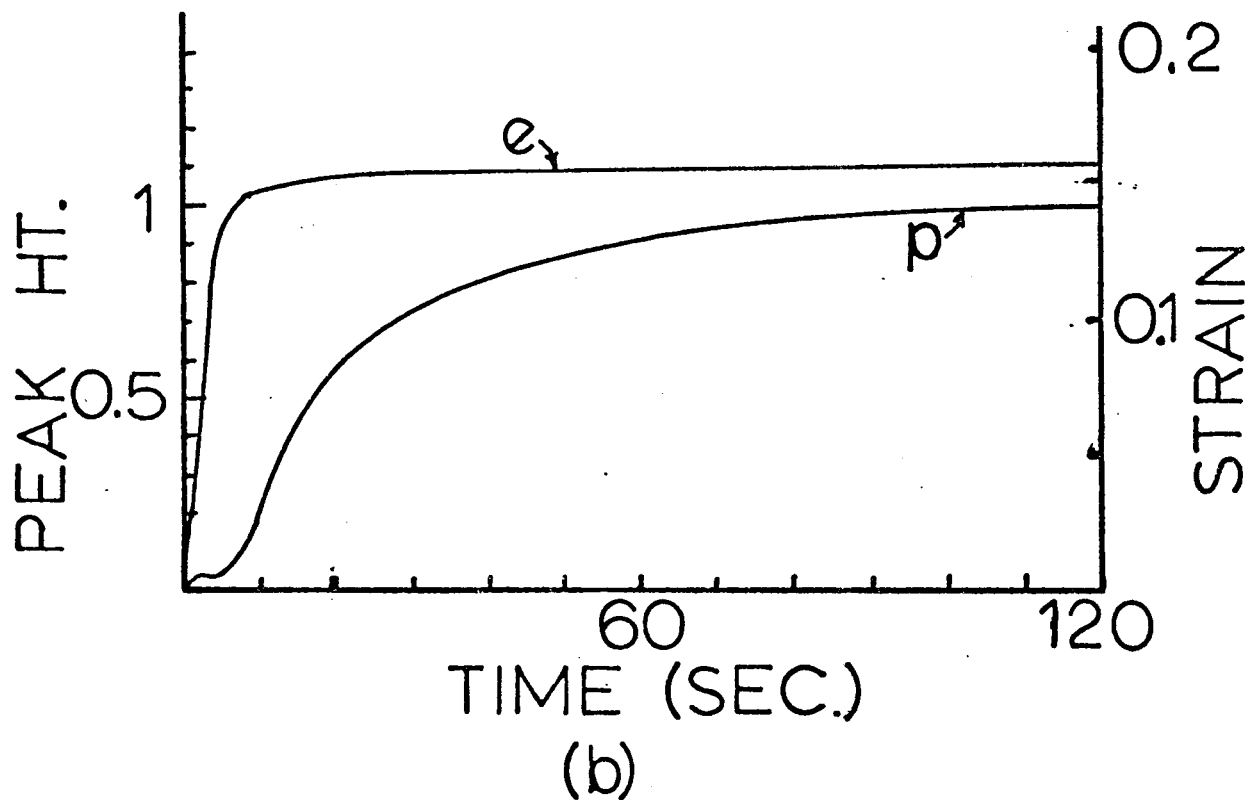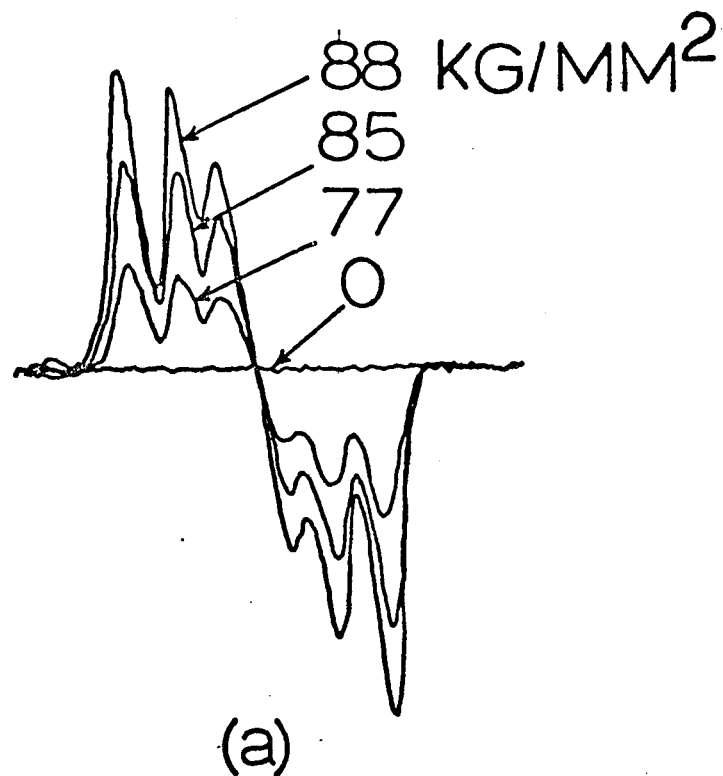
Figure 14. EPR spectra during tensile loading leading to fracture in air at room temperature.
(a) Equilibrium concentration of free radicals at the stresses indicated.
(b) Strain at a constant load of 86 kg/mm^2 (based on original area) versus time. Increase in height of first peak in above spectra versus time.